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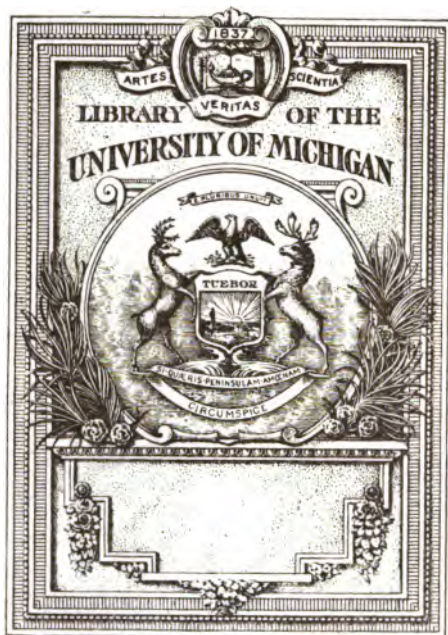
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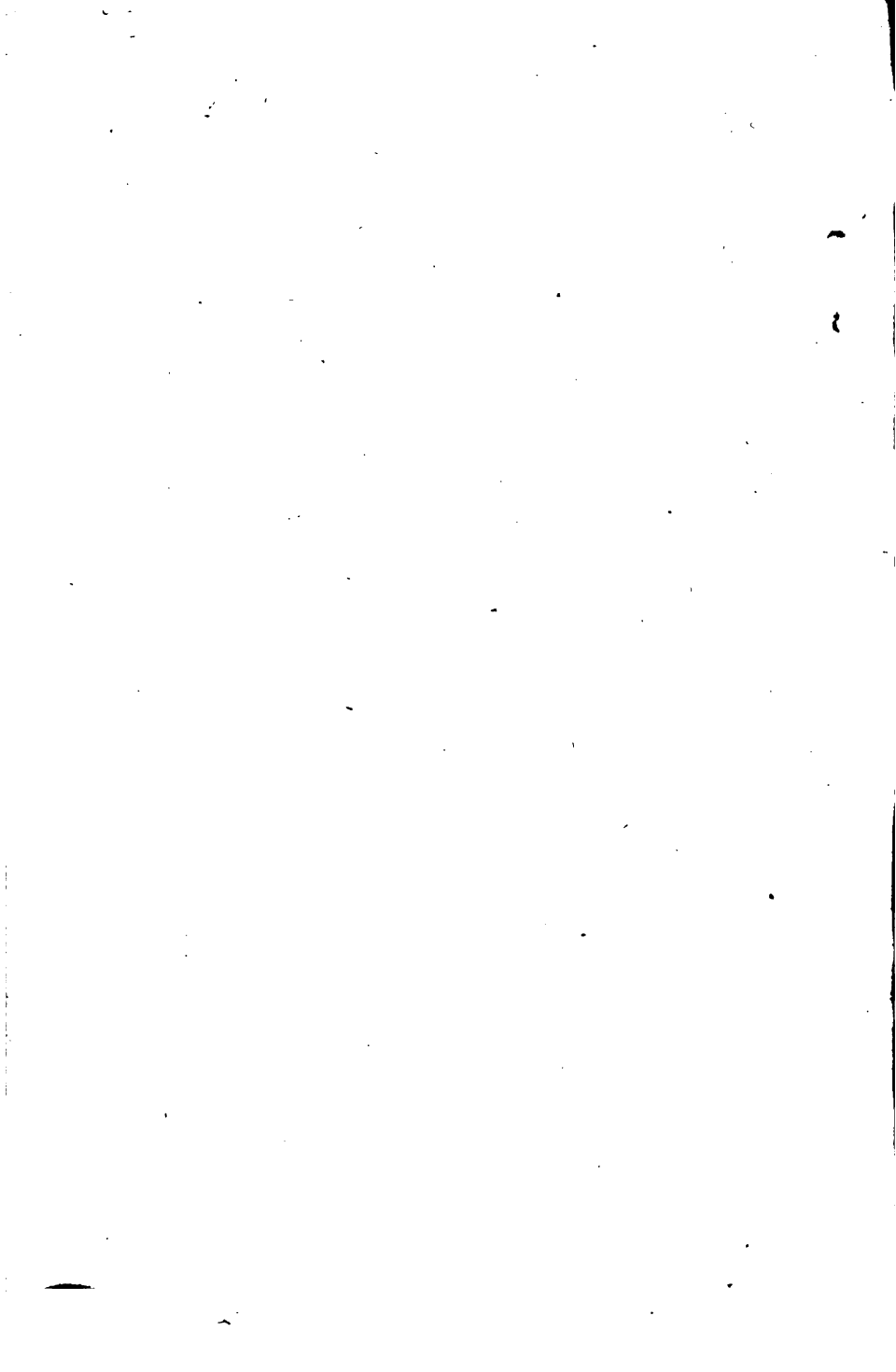


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THE AFFINITY OF CERTAIN  
COMPOUNDS

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AS EXPRESSED IN TERMS

OF

ELECTROMOTIVE FORCE

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A T H E S I S

PRESENTED BY

M. J. THOMPSON, A. B.

CANDIDATE FOR THE DEGREE OF MASTER OF ARTS

1884

(UNIVERSITY OF MICHIGAN)



## A THESIS.

The investigations narrated in the following paper were undertaken at the suggestion of Professor J. W. Langley, and throughout the work I have enjoyed the benefit of his counsel.

The relation of electrical to chemical forces has been a favorite subject of study with chemists and physicists for a long time, even with those who did not believe in the identity of nature in these two forms of energy.

As late as April 5, 1881, Prof. Helmholtz<sup>1</sup> in his Faraday Lecture advocates the doctrine that these forces are fundamentally identical. After discussing Faraday's law of definite electrolytic action and its results, he says:

"Faraday very often recurs to this to express his conviction that the forces termed chemical affinity and electricity are one and the same. . . . I think these facts leave no doubt that the very mightiest among chemical forces are of electrical origin."

It will be seen even in the following pages that chemical forces may be measured and expressed in terms of electrical measurement, without any computations or conversions whatever. This fact certainly does not prove the identity of the two forces, but it is an interesting fact and one not to be overlooked in making up one's mind on the subject.

This attempt to get some numerical data as to the relative strength of attractions in chemical affinities is not a late effort only with workers in physical science.

Tidy<sup>2</sup> enumerates six methods that have been employed by different investigators, and which I transcribe, giving the name of one or more of the principal experimenters by each method.

I. Affinity measured by reference to the specific gravity of bodies. (La Place and others.)

II. Affinity measured by the force of adhesion. (Guyton Morreaux.)

III. Affinity measured by the amount of force required to effect the decomposition of a compound. The decomposition was effected in this case, first—by heat; secondly—by a superior affinity.

<sup>1</sup> *Popular Science Monthly*, June, 1881.

<sup>2</sup> *Handbook of Modern Chemistry, Inorganic and Organic*, by Charles M. Tidy. pp. 14-19.

IV. Affinity measured by the time of combination. (Wenzell.)

V. Affinity measured by the combining proportions. (Kirwan.)

VI. Affinity measured by the electrical condition. (Thompson.)

In this method the "electrical condition" is shown by the successive precipitations.

It is not within the scope of this article to enter into a discussion of the merits of these various methods; suffice to say that Prof. Tidy closes his review by saying:

"Summarizing these facts we may note, first, that we have no means of measuring affinity absolutely, and secondly, but very uncertain means of estimating it relatively."

VII. Another way of approaching this subject not included in the above list was first indicated by Joule<sup>1</sup> in the following words:

"I take a glass vessel filled with a solution of an electrolyte and properly furnished with electrodes; I place the electrolytic cell in the voltaic circuit for a given length of time and carefully observe the decomposition and the heat evolved. By the law of Ohm I then ascertain the resistance of a wire capable of obstructing the current equally with the electrolytic cell. Then by the law we have proved [i.e., Joule's law] I determine the quantity of heat which would have been evolved had a wire of such resistance been placed in the current instead of the electrolytic cell. This theoretical quantity being compared with the heat actually evolved in the electrolytic cell is always found to exceed the latter considerably."

"The difference between the results evidently gives the amount of heat absorbed during electrolysis, and is therefore equivalent to the heat which is due to the reverse chemical combination or other means."

This method has of late been employed by several experimenters, prominent among whom is C. R. Alder Wright,<sup>2</sup> who in a series of articles has discussed the results obtained by himself and others.

Without doubt this is one of the most truly scientific methods that has yet been employed and the results obtained by it are very instructive, but it seems to me that the difficulties of manipulation would be very great and the errors of observation would be liable to be large.

VIII. Another method much used of late and probably more available than any of the preceding is to measure the heat evolved during the combination of elements.

Thus, the heat evolved by the oxidation of a metal (as determined by burning it in an atmosphere of oxygen) evidently gives some indication of the absolute force binding together the atoms of metal and oxygen.

Or, if we dissolve the metal in an acid the amount of heat evolved will evidently give an expression for the affinity between the acid radical and the metal.

<sup>1</sup> *Philosophical Magazine*, [4] p. 481.

<sup>2</sup> See *Philosophical Magazine* for 1880-1-2.



This field has been cultivated industriously especially by Favre and Silberman, Berthelot and others, and extended tabulated results published.

IX. Still another method is the one employed by myself, and which, as far as I can learn, no one has hitherto used. The principle of it may be explained as follows:

The atoms or groups of atoms of a molecule are held together by a certain force of chemical affinity. This attraction, we know, can be overcome by the electrical current and the atoms torn asunder. We also know that below a certain electro-motive force this separation does not occur. Now could we measure the electro-motive force of the current at the moment this separation first takes place, we would, evidently, have an expression for the strength of the chemical affinity which has been overcome. But if the battery current be now broken and the wires from the electrodes be connected, we find a reverse current generated by the recombination of the separated elements, and we may rationally assume that its electro-motive force is just equal to that which was necessary to separate the elements. But it must be remembered that a molecule is not always broken up into the individual elements that compose it, but often into groups of atoms only, when, of course, the electro-motive force of the polarization current will be different from what it would be in the first case. The fact is, when this proximate analysis, as it might be called, occurs, rather than the ultimate, the electro-motive force of the polarization current will be lower, for were the latter action the easier it would occur first.

Again, were the elements, or Ions, as they are called, able to unite with the electrodes at the moment of separation, evidently there would be no current of polarization at all, and any such action that may occur will have the effect of reducing the electro-motive force of the current.

I will now describe the various parts of the apparatus employed, how they were put together, and the methods of manipulation.

## I. THE BATTERIES.

a. The battery employed was a new one, invented by MM. de La Sande and Chaperon.<sup>1</sup>

As I used it, it was essentially as follows. The battery in appearance and action resembles the common gravity battery, but, in place of the solution of copper sulphate the cell was filled nearly to the top with a saturated solution of commercial concentrated lye.

<sup>1</sup>For various forms of this cell see *The Electrical World*, September 1, 1883.

This dissolved the Zinc, which was suspended as in the gravity cell. But in place of the copper plate of this latter cell a copper or iron dish was used, being filled with the black oxide of copper, which yielded up its oxygen to form water with the hydrogen evolved at the zinc plate, and thus prevented polarization of the battery.

Air must be excluded from the solution to prevent its absorbing carbon dioxide from the atmosphere of the room and thus becoming neutralized. This is easily accomplished by setting up the battery quite warm and scattering pieces of paraffine on the liquid, which melt and spread over the surface, and, on cooling, form an air-tight layer.

The inventors give the electro-motive force of this cell as .98 of a volt, though, as will be seen farther on, it was not necessary for me to know either the electro-motive force or the internal resistance; the latter, however, I know to be quite low.

This battery I found to be a very serviceable one, giving a current that was very constant, though often kept on a closed circuit for a whole afternoon, while it could be left on an open circuit for seemingly any length of time.

*b.* For measuring the difference of potential between the ends of the Rheostat wire I used the well known Clark's Standard Cell, in a way to be described. Before my investigations were quite finished some sort of decomposition seemed to occur in the paste of this cell, so that I did not place much reliance on the accuracy of its electro-motive force, as the different cells did not agree among themselves. This unfortunate circumstance vitiates the numbers given for silver and mercury especially.

## II. THE GALVANOMETERS.

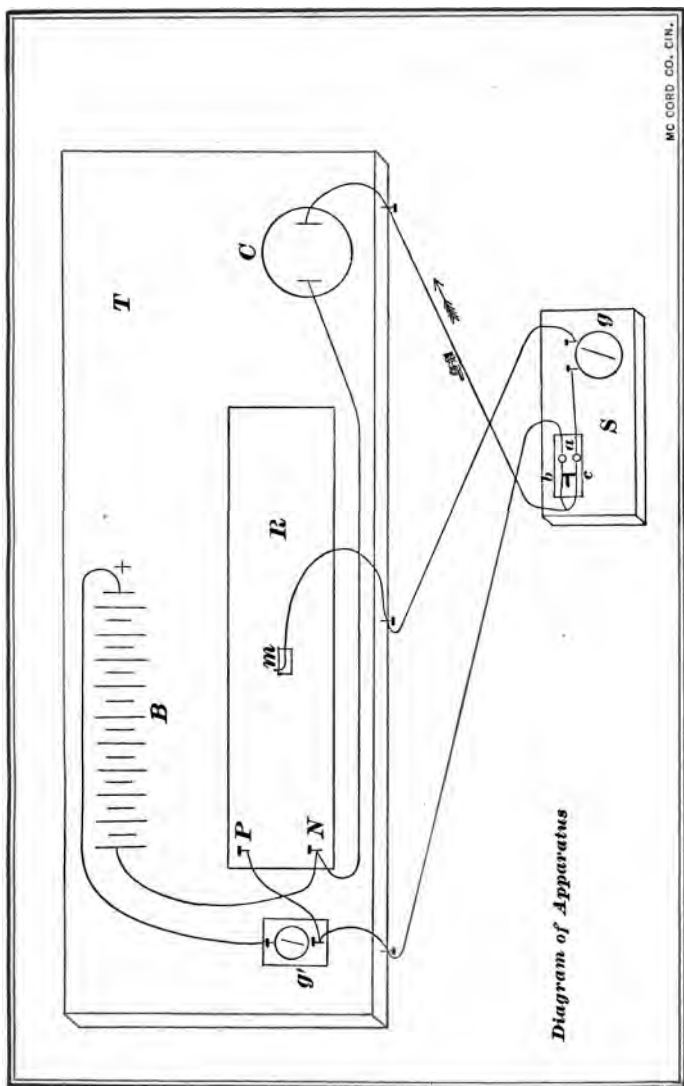
*a.* The galvanometer *g*, page 11, was a fine astatic needle instrument. It was very delicate, as I found by various tests that I applied.

*b.* The one marked *g'* was an ordinary instrument, not at all delicate, and kept in the circuit all the time to detect any change in the strength of the current during the progress of an experiment.

## III. THE RHEOSTAT.

This will be readily understood by referring to the figure on page 13. A board about 40 centimeters wide and something over a meter long was planed smooth and strengthened by cleats placed on the under side and which also served as supports.

Across the upper side of the board two lines were drawn at right angles to the edge of the board and just one meter apart.



The intervening distance was next divided into centimeters by lines drawn parallel to these first lines. A narrow strip of paper was then glued along one edge of the board and the lines numbered upon it from 0 to 100, beginning at the left.

The whole was at last covered with a coating of shellac varnish to prevent the absorption of moisture and consequent warping.

A number of bits of copper about two centimeters wide and three long were then cut from sheet copper. Ten of these were placed along the first line at the left hand side, with their inner edges just touching it, and 5 or 6 *mm* apart. Nine pieces were similarly placed at the other end of the board, but with their middle points just opposite the spaces of the other row.

Eighteen copper wires were stretched between these pieces of copper after the manner represented in the drawing (the number of wires being reduced however) and soldered fast at the ends. This wire was about 6.9 mils in diameter and had a resistance, according to my measurement, of .67 ohm to the meter.

To the pieces of copper *P* and *N* binding-posts were attached, which thus became the poles of the Rheostat.

By this arrangement I evidently had before me eighteen meters of wire, whose resistance in various parts of its length for equal spaces was equal, as I found by measurement.

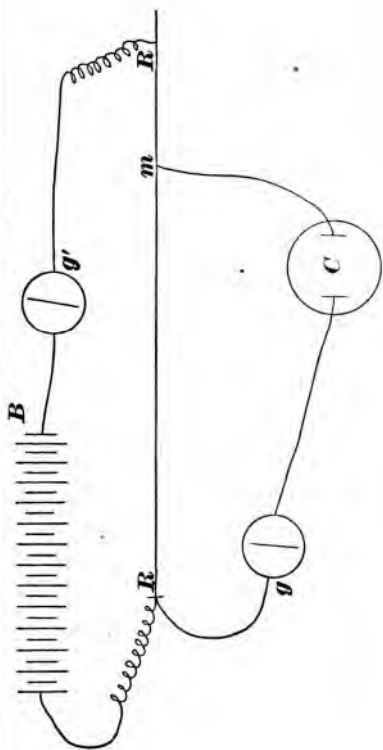
Now suppose a current is flowing through the wire from the positive pole *P* to the negative pole *N*, and that the difference of potential between the two poles is three volts, as I have found by measurement.

If I place a finger of one hand upon the negative pole and a finger of the other hand upon the wire at the end of the twelfth meter, counting from the negative pole, I have evidently taken off a part of the current which is flowing through the wire, and the electro-motive force of the part so taken off is two volts, for the difference of potential varies gradually from 0 at the negative pole to 3 volts at the positive pole, and as I have taken off two-thirds of the wire I have evidently taken off two-thirds of the whole electro-motive force.

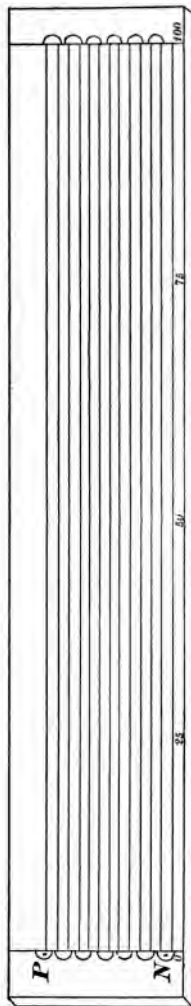
The movable block *m*, page 11, was for the purpose of making this sliding connection. As I could measure to centimeters, I could thus measure to the one eighteen-hundredth of the whole difference of potential between the poles.

#### IV. THE ELECTROLYTIC CELL.

*a.* For the cell itself a small beaker was used. This was generally set in a larger, thicker one and which was also slightly taller and



*Theoretical Diagram*



*Rheostat*

thus could act as a support to the pieces of wood to which the electrodes were attached.

The space between the two beakers could be filled with ice or snow when low temperatures were desired.

When high temperatures were desired the cell was placed in a water-bath beneath which a lamp could be lighted.

Sometimes the bath itself was packed with snow around the cell, and which could thus gradually be raised from perhaps  $1^{\circ}\text{C}$  to  $94$  or  $96^{\circ}\text{C}$ .

I found that a liquid thus placed in a water-bath would generally not rise above  $94^{\circ}\text{C}$ .

At the altitude of Ann Arbor water boils below  $100^{\circ}\text{C}$  anyhow.

*b*. Platinum electrodes were generally used. These were thin plates, about 2 centimeters wide and 3 long.

One end of the plate was folded tightly over a thin platinum wire which, to give it rigidity, was passed through a very small glass tube, and this latter was fastened to a piece of wood for a support.

Before using the electrodes they were cleaned with acids, washed in pure water, and generally ignited for some time.

In the electrolysis of chlorides I found that the liberated chlorine united with the platinum electrode, hence, in working with these compounds I had to use carbon electrodes. These were sticks of common gas carbon something less than a quarter of an inch square. Before using them they were boiled for several hours in hydrochloric acid to remove any metals they might contain.

In working I did not measure the distance between the electrodes, but aimed to keep it about the same—something less than 2 centimeters.

The apparatus was set up as shown in the diagram on page 11, of which *T* is a long table on which were placed the battery *B*, the rheostat *R*, the electrolytic cell *C*, and the coarse galvanometer *g'*.

*S* is a smaller stand holding the fine galvanometer *g*, and the double key *a*.

The whole was connected as shown in the diagram, the wires running from one table to the other being covered with a coating of shellac varnish and fastened to the floor.

Now, supposing that everything is in readiness, the arm *b* of the double key *a* is depressed and the wire dips into the corresponding mercury cup; and this, it will be seen, sends a current into the cell in the direction of the arrow.

But if the other arm be now depressed (which at the same time

makes the connection through the galvanometer) we find the current of polarization flowing through the wire in the direction of the hand. But the current from the rheostat is likewise flowing through the galvanometer in the direction of the arrow.

If these two currents be just equal they will neutralize one another and the galvanometer will not be deflected. By a series of tentative efforts, made by changing the position of the point where the block touched the wire, this neutral point was soon found.

The polarization current, however, maintained its strength but for a few moments, after which it rapidly ran down, hence, only the first throw of the needle could be considered.

At first glance it might appear that the galvanometer was used to compare electro-motive forces. But a little study will show that it was used to measure neither strength of current nor electro-motive force, but it was used merely to indicate the absence of any current, hence, the absence of any electro-motive force.

Knowing the difference of potential between the ends of the rheostat wire it was easy to compute the electro-motive force of the polarization current.

Thus: Let  $a$  = Difference of potential.

Let  $d$  = Length of wire, counting from  $N$  to  $M$ .

Hence,  $\frac{a}{d} = x$  = The E. M. F. taken off the rheostat, = the E.

M. F. of the polarization current.

In a similar manner the difference of potential between the poles of the rheostat could be estimated by placing one or more of Clark's Standard Cells in place of the electrolytic cell, so that the current from this battery flowed in the same direction as the polarization current did.

Now, Let  $n$  = number of Clark's cells employed.

Let  $d$  = distance on rheostat wire from  $N$  to  $M$ .

Whence,  $\frac{1.457 \times n}{d} = x$ , where  $x$  = difference of potential.

I now desire to present a table of electro-motive forces of various substances as determined by this method.

When in the following table the name of the electrode is followed by the symbol of a metal, it means that during electrolysis the metal was precipitated on the negative electrode.

The numbers given are the result of single determinations. Doubtless the mean of many observations would give more accurate and satisfactory results. Most, however, if not all, were re-determined when I found that the numbers varied but slightly from those here given,

Name of Salt.	Kind of Electrodes.	E. M. F. at 16° to 20° C.	E. M. F. at about 94° C.	Per cent. of Fall of E. M. F.
MgCl <sub>2</sub>	C & C	2.64	2.25	17
CaCl <sub>2</sub>	C & C	2.77	2.17	21
NaCl	C & C	2.86	2.54	11
KCl	C & C	2.90	2.65	9
HCl	C & C	1.83	1.68	8
BaCl <sub>2</sub>	C & C	3.00	2.59	13
FeCl <sub>2</sub>	C & Fe	1.92	1.64	14
MgSO <sub>4</sub>	C & C	2.90	2.39	18
ZnSO <sub>4</sub>	Pt & Pt (Zn)	2.64	2.31	13
CdSO <sub>4</sub>	Pt & Pt (Cd)	2.47	2.30	6
FeSO <sub>4</sub>	C & Fe	2.01	.82	59
CuSO <sub>4</sub>	Pt & Pt (Cu)	1.62	2.39	14
HgSO <sub>4</sub>	Pt & Pt (Hg)	1.59	1.19	31
Ag <sub>2</sub> SO <sub>4</sub>	Pt & Pt (Ag)	1.25	1.04	17
Cu(NO <sub>3</sub> ) <sub>2</sub>	Pt & Pt (Cu)	1.55	1.36	12
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Pt & Pt	2.22	1.65	25
KHCO <sub>3</sub>	Pt & Pt	2.44	1.59	34
H <sub>2</sub> O	Pt & Pt	2.13	1.86	12

### AFFINITY.

So far I have used the word "affinity" in the popular acceptance of the term as meaning the attraction between the atoms of different elementary bodies resulting in the formation of new chemical compounds; and that this form of attraction, differing from gravitation, acts only at insensible distances.

But we know that the value of this force may be changed by varying the conditions.

Two views have naturally flowed from this observed fact.

*First.* We may look upon the atom as having stored up within it a certain inherent amount of attractive force which never changes, and that any apparent change arises solely from the fact that an opposing force has intervened, and that it is the excess over this only that we observe; or *Second.* We may look upon the atom as not having any absolute amount of attractive force peculiar to it, and that any such force that it does exhibit at any time is simply the resultant of the many conditions that surround it. But we desire a theory more dynamical in its nature, and which will yield itself to precise reasoning.



This affinity is evidently a form of energy; if so it may be expressed by the formula  $\frac{1}{2}mv^2$ —a function of mass and velocity ( $m$ , however, is a constant).

The relative mass of the atoms we know—their atomic weights—and these do not change.

The velocity we do not know, and it is, moreover, liable to change. Suppose, now, to any molecule a given amount of force is imparted. It may all appear as a vibration of the molecule as a whole—hence it will affect surrounding bodies, in fact it appears as heat, electric current, etc., or, the force imparted may only have the effect of setting up internal vibration of the component atoms, consequently will not affect surrounding bodies, in short it becomes latent heat, or potential energy.

As we have seen, the energy of this system of atoms is a function of its mass and the mean velocity of its parts.

The fact that no two atoms have the same weight would immediately suggest that no two atoms have the same inherent energy—other things being equal.

But we know that other things are not equal, for, the strength of affinity is not directly proportional to the atomic weight.

But it is possible that the mean velocity of the system should be so correlated to the mass that the energies of all elements should be equal.

But we know that such a correlation does not exist, for all atoms do not have the same strength of affinity. Thus we see that two quantities go to make up affinity—a constant and a variable. Hence we come to these conclusions:

I. It can not be said that an atom has a fixed total quantity of energy inextricably locked up with it, for a variable quantity is involved.

II. It can not be said that the energy (or affinity) of an atom depends solely upon the conditions that surround it, for a constant quantity peculiar to itself is involved.

Could an atom of each of the elementary bodies be isolated and placed under absolutely the same conditions that surround all the others, and the energy of each determined, we would have an expression for its energy or affinity compared with all the others.

Thus we see that two atoms may have the same strength of affinity, but not under the same conditions, as the constant factor involved (the atomic weight) is in no two cases the same.

Thus far I have used the words atom and molecule interchange-

ably, but perhaps a word on this point is necessary. It might be objected that while the principle applies well enough to molecules in which internal movements can take place, and hence latent heat exists, yet in the case of the monatomic elements there could be no such thing as latent heat.

If we look upon an atom as absolutely a unit, inflexible, not made up of parts, or, if so made up that the parts never change their relative positions, then, if atoms act as individuals only, the objection is a valid one.

And it is true that in the processes of the laboratory such seems to be their constitution,—they are never broken up into component parts.

But there are physical reasons for modifying this view, and it will be seen that in this discussion the words atom and molecule may be used interchangeably, for the atom of systematic chemistry itself becomes a molecule.

Now to apply these principles to the subject in hand.

Two atoms each have a certain amount of energy stored up within themselves. They combine to form a molecule. The internal vibration of each is reduced; but this energy appears as a vibration of the molecule as a whole; it is manifested as heat, electric current, etc.

To separate these two atoms again as much energy must be imparted to them as they gave up when they came together.

This energy may be imparted as heat and gives the phenomenon of dissociation, or, it may be imparted by the electric current and gives the phenomenon of electrolysis.

I desire now to refer to the work of well-known investigators in this field of measuring affinity, and among them there are none better known than Favre and Silberman. I take the data as collated by Sprague.<sup>1</sup>

But before comparing them with the numbers obtained by myself, a few words of explanation are necessary.

I. As I understand the experiments of these investigators, the substances were used in the solid state, excepting, of course, those which are gases at the ordinary temperatures.

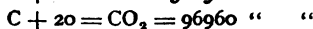
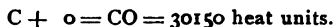
But we know that considerable energy is evolved or absorbed in changing a substance from a liquid to the solid or to the gaseous state.

We have an illustration of the energy expended in changing a

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<sup>1</sup> *Electricity; Its Theory, Sources and Applications.* By John T. Sprague.

body from the solid to the gaseous state in the successive oxidations of carbon.



It is but reasonable to suppose that the affinity of the carbon for the first atom of oxygen is as great as it is for the second; and we see how large a share of the energy set free by the first combustion is expended in changing the carbon from a solid to a gas.

II. As throwing some light upon the results obtained with salts in the solid state compared with those in solution, I transcribe some numbers given by Berthelot.<sup>1</sup>

Heat disengaged, in calories.

Salt.	In Solid State.	In Solution.
KCl	105.0	100.8
NaCl	97.3	96.2
CaCl <sub>2</sub>	81.1	93.8
MgCl <sub>2</sub>	75.5	93.5
FeCl <sub>2</sub>	41.0	50.0

To my mind these considerations do not explain why the numbers obtained by the method I used are larger than the numbers given in the books. But whatever may be the explanation of it the results I obtained are remarkably consistent among themselves, and one can place some reliance upon them in foretelling results.

III. Sprague generally gives the data in foot-pounds, but in the table to which I refer (p. 214) they are also given in "equivolts"—a term originated by himself. He defines it as "the force engaged in effecting one equivalent of chemical action in a circuit of one ohm resistance, and under the volt electro-motive force."

He defines a "chemic" to be a "rate of current which in a second is equal to .17606 of a veber, and would in ten hours deposit or set free one equivalent in grains of any element or iron."

The value of the "equivolt" is 4673 foot-pounds. It will be seen that his numbers express energy, while mine express intensity—the element of time is not involved. Hence for the purpose of comparison the equivolt may be taken as equal to the volt.

It will be seen that the chlorides are higher than the sulphates. This is because he makes an allowance for the formation of water

<sup>1</sup> *Essai de Mécanique Chimique* par M. Berthelot, Tome Premier, p. 378.

when an oxide dissolves in  $\text{HCl}$ , but does not make this correction in the case of  $\text{H}_2\text{SO}_4$ , saying that the real energy of the formation of  $\text{SO}_3$  is not known. Hence, for purposes of comparison, I have added a column (No. 4), deducting this correction from the chlorides.

I.	II.	III.	IV.
Base.	Sulphates Equivolts, E. M. F.	Chlorides Equivolts, E. M. F.	Chlorides (adapted) Equivolts, E. M. F.
Copper.	1.258	1.467	.770
Hydrogen.	1.919	1.707	1.010
Iron.	2.069	2.268	1.571
Zinc.	2.248	2.400	1.703
Sodium.	3.795	3.996	3.318
Potassium.	3.913	4.121	3.424

The data given in the table on page 16, together with the results of other experiments to be narrated in the proper place will, I think, leave no doubt as to the truth of the following propositions.

With each proposition I will give all the data bearing on the subject.

#### PROPOSITION I.

*Substitutions between salts take place in the order of the relative magnitude of their electro-motive forces.*

$\text{MgCl}_2$ 2.64	$\text{FeCl}_2$ 1.92
$\text{MgSO}_4$ 2.90	$\text{FeSO}_4$ 2.01
$\text{Cu}(\text{NO}_3)_2$ 1.55	$\text{NaCl}$ 2.86
$\text{CuSO}_4$ 1.62	$\text{KCl}$ 2.90

The inference from these data does not need any special exposition. In each case it will be seen that the sulphate has a higher electro-motive force than is found in either the corresponding chloride or nitrate. This is in accord with the well known fact in qualitative chemistry, that sulphuric is one of the strongest acids, and will displace most others from their salts.

This field of investigation will, I think, prove a very fertile one when cultivated more thoroughly by scientific chemists.

Some day, no doubt, elaborate tables will be made out, giving the numerical data (in E. M. F., or otherwise) as to the affinity between the elements of various salts, so that one can make out the reaction by examining the magnitude of the affinity.

One must not forget, however, that the affinity alone does not determine the reaction.

For example, the relative quantity of the salts present has a large influence.

Thus if to a solution of equal parts of KOH and NaOH we add just enough HCl to unite with all the K, it does not all unite with that base, but part of it goes to the Na, and, neglecting numbers, we have a reaction something as follows:



### COROLLARY.

*A metal can not dissolve in an acid unless the free acid has a lower electro-motive force than the corresponding salt of the metal.*

This follows directly from the above proposition if we define an acid to be "salt of hydrogen," when it becomes simply a case of substitution between salts.

CuSO <sub>4</sub> 1.62	CdSO <sub>4</sub> 2.47
HgSO <sub>4</sub> 1.59	ZnSO <sub>4</sub> 2.64
Ag <sub>2</sub> SO <sub>4</sub> 1.25	FeCl <sub>2</sub> 1.92
MgSO <sub>4</sub> 2.90	H <sub>2</sub> SO <sub>4</sub> 1.90
FeSO <sub>4</sub> 2.01	HCl 1.83

Here Mg, Zn, Cd, and Fe are soluble in H<sub>2</sub>SO<sub>4</sub>, while Ag, Hg, and Cu are not. The table also shows why iron dissolves in hydrochloric acid.

Why Ag, Hg, and Cu should dissolve in hot, concentrated sulphuric could, perhaps, be explained by a further examination of the influence of heat.

It will be noticed that at the boiling point the electro-motive force of the iron sulphate and chloride is lower than that of the corresponding free acid.

This, I think, can be explained as follows: The ferrous salts by being boiled in the open air were largely oxidized to the ferric condition; they gave every indication of such change.

Hence I was measuring the ferric salt, and the fact that its electro-motive force is lower than that of the corresponding free acid shows that a ferric salt can not be formed directly by dissolving the metal in the acid, for this will always form the ferrous salt, and the ferric condition is the result of an after change.

## PROPOSITION II.

*The electro-motive force of a compound falls with the rise of temperature.*

An examination of the data given on page 16, shows that there are no exceptions to this law among the salts upon which experiments were made.

The phenomenon of "dissociation" would lead us to expect such a result as the table shows; and the principles involved in this phenomenon I have discussed under the head of "affinity."

The considerable per cent. of fall of some of these salts shows that, with them this breaking up occurs at quite moderate temperatures.

Could a curve be made out illustrating this decline and its equation determined, this point of dissociation might be calculated.

But very accurate measurements must be obtained to make out this curve with exactness; while the carrying of such curves illustrating physical phenomena beyond the point of actual observation is of doubtful propriety, as later and more extended experiments often prove that they have been very misleading.

However, I will give the results of three experiments I tried with reference to this point.

The cell, filled with a saturated solution of  $\text{CuSO}_4$ , was placed in a water bath, packed around with snow and  $\text{NaCl}$ , and the electro-motive force measured as the temperature was gradually raised by a lamp placed beneath, Table I.

A similar experiment was tried with the cell filled with pure re-distilled water, Table II.

I.		II.	
Temperature.	E. M. F.	Temperature.	E. M. F.
$1\frac{1}{2}^{\circ}\text{C}$	1.62	$1^{\circ}\text{C}$	2.22
19	1.58	15	2.13
$36\frac{1}{2}$	1.51	31	2.09
54	1.45	44	2.06
$69\frac{1}{2}$	1.42	$54\frac{1}{2}$	2.03
80	1.39	74	1.90
93	1.38	93	1.86

The intervals here are irregular; but they are constant enough for us to see that the curves for these two substances would not differ materially, though they make it probable that the curve for  $\text{CuSO}_4$  would touch the axis of abscissas sooner than the other would.

The resistance of pure water was so great and current so reduced that the action was feeble and indistinct. So I used acidulated water, and otherwise modified the next experiment.

The water was placed in a U-tube and the wires from the electrodes hermetically sealed in the ends.

Also to raise the boiling point of the water in the bath surrounding the cell it was saturated with  $\text{CaCl}_2$ .

This arrangement gave the following results:

Temperature.	E. M. F.	Temperature.	E. M. F.
1°C	1.91	96°C	1.70
25	1.84	125	1.65
50	1.79	143	1.60
75	1.75	159	1.55

Neglecting the influence of the pressure of the aqueous vapor I have drawn a curve illustrating these results. (See page 24.) Its equation, however, I was not able to make out.

Considering it a straight line, and it does vary greatly from that, it gives the point of dissociation for water at 896°C.

In Watt's<sup>1</sup> dictionary incipient dissociation is said to occur at 960°C.

Here, for the sake of the proximity of the illustrations, and not from any organic connection with the line of thought, I insert an account of some experiments on related subjects.

I. When we mix water and  $\text{H}_2\text{SO}_4$  a large quantity of heat is evolved. This indicates to us that they have not simply mixed, but that the water molecules and acid molecules have united in some way.

I took 20 c. c. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) and boiled it until fumes were given off, then allowing it to cool I measured its E. M. F., and added varying quantities of water successively as shown in the table, allowing the mixture to cool each time before measuring.

20 c. c.  $\text{H}_2\text{SO}_4$  + 0 c. c.  $\text{H}_2\text{O}$  = 1.84 sp. gr. = 1.88 E. M. F.

20        "        + .5        "        = 1.78        "        = 1.96

20.5        "        + 1.        "        = 1.74        "        = 1.87

21.5        "        + 1.        "        = 1.71        "        = 1.83

22.5        "        + 1.        "        = 1.68        "        = 1.82

23.5        "        + 1.        "        = 1.65        "        = 1.83

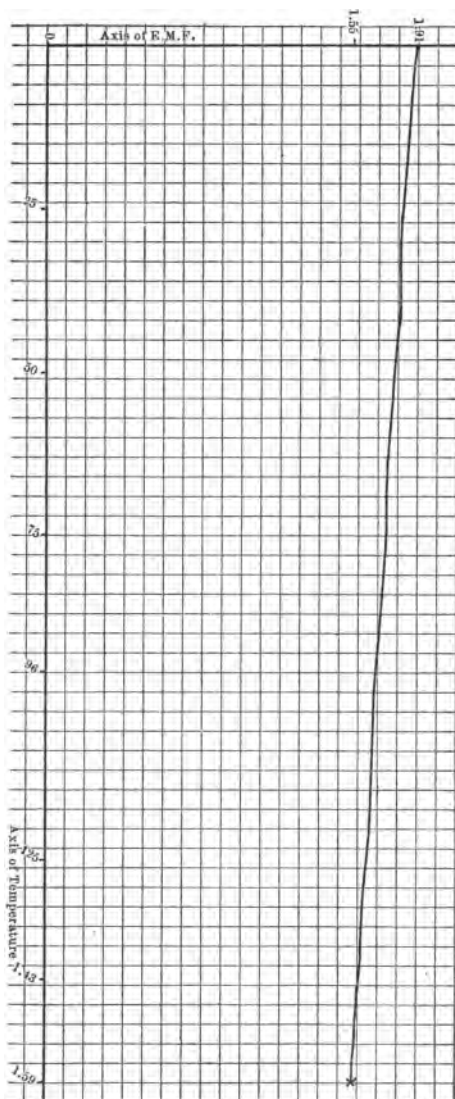
24.5        "        + 10.        "        = 1.46        "        = 2.05

34.5        "        + 10.        "        = 1.36        "        = 2.02

44.5        "        + 10.        "        = 1.29        "        = 1.94

Acidulated water = 1.80 E. M. F.

<sup>1</sup>Watt's *Dictionary of Chemistry*, First Supplement—Art. Chemical Action.





I have drawn a curve (page 26, No. 1) illustrating these results. This wavy line seems to indicate that as water is added to  $\text{H}_2\text{SO}_4$  there are a succession of compounds of water and acid molecules of a varying degree of stability, requiring various degrees of force to break them up.

I thought perhaps a curve showing the resistance of water at various degrees of dilution might show a similar fluctuation, but I find on examination that there is no resemblance whatever between the two curves.

I take some data as given by Maxwell.<sup>1</sup> The numbers are illustrated by a curve on page 26, No. 2.

Sp. gr. of $\text{H}_2\text{SO}_4$ at 18.5 C.	Resistance at 22°C. Hg = 1.	Sp. gr. of $\text{H}_2\text{SO}_4$ at 18.5 C.	Resistance at 22°C. Hg = 1.
.99	764300	1.26	13132
1.00	465100	1.31	14286
1.05	34530	1.35	15762
1.09	18946	1.39	17720
1.14	14990	1.43	20796
1.20	13133	1.50	25574

It will be seen that the curves are entirely dissimilar.

II. In measuring the E. M. F. of a salt in solution I always aimed to have the solution saturated, but I found that this was not a matter of great importance.

A saturated solution of

NaCl	diluted to 20 volumes	fell .06 of a volt.
KCl	" 20 "	" .13 " "
$\text{CaCl}_2$	" 20 "	rose .06 " "
$\text{CuSO}_4$	" 600 "	remained constant.

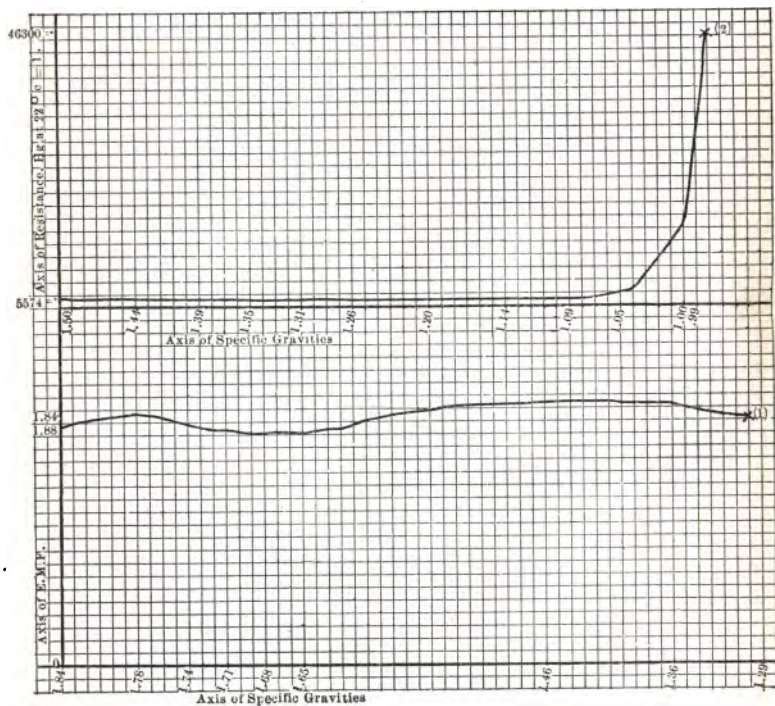
### PROPOSITION III.

*The electro-motive force of a salt in solution rises as the pressure upon the solution is increased.*

This experimental result might have been anticipated from these two considerations.

*First.* In electrolysis the oxygen and hydrogen (of the water used) pass into the gaseous state, in which change, as we have seen, they absorb energy.

<sup>1</sup>A Treatise on Electricity and Magnetism, by J. Clerk Maxwell. Vol. 1. p. 44.



*Second.* The pressure tends to keep them in the liquid condition, hence an augmented force is necessary to overcome this tendency.

In the experiments a glass U-shaped tube was partially filled with acidulated water. Platinum wires with foil upon their ends were then inserted at each end of the tube and hermetically sealed. The enclosed gases thus set free by electrolysis supplied the pressure. This was measured by a small mercurial manometer placed in the tube.

The slightly rarified condition of the enclosed air, owing to the condensation of the vapor generated when the tube was sealed, often, however, lifted the mercury out of the tube, and also, after the pressure had risen to 7 or 8 atmospheres, the indications of the manometer could not be made out.

For these reasons I depended rather upon the time between two readings during which the gases had been generating—hence the hour of the day at which the readings were taken is given.

To increase the quantity of gas generated, a Bunsen battery, of a varying number of cells, was so placed as to send its current through the electrolytic cell in the same direction as the general battery, ("B," page 11.) This additional current could be cut off at pleasure, and was so disconnected just before readings were taken.

These experiments were tried several times, but I transcribe the results of the last two only, as all were similar. "I" is given in pairs.

I.			II.		
Battery Used.	Time.	E. M. F.	Battery Used.	Time.	E. M. F.
"B"	11.17 a.m.	1.86 <sub>1</sub>	"B"	3.32 p.m.	1.85
"	11.23	1.92 <sub>2</sub>	"	3.40	1.91
			"	3.45	1.91
"	11.25	1.92	"	3.54	1.94
"	11.35	1.96 <sub>3</sub>	"	4.00	1.94
Added 2 Bunsen cells.			"	4.17	1.96
	11.45	1.96	"	4.33	1.97
	12.05	1.96 <sub>4</sub>	"	4.48	1.86
Added another Bunsen cell.			"	5.05	1.86
	12.05	1.96	Added a Bunsen cell.		
	12.25	1.78		5.33	1.69
			Added a Bunsen cell.		
1. About 1 atmosphere by manometer.				5.38	1.66
2. " 2 atmospheres "		"			
3. " 4 " "		"			
4. " 8 " "		"			

Though another cell was added to "II" it made no appreciable change in the result.

The gradual rise is easily explained on the principle recalled a few minutes ago.

The sudden fall is not so easily explained, but doubtless it was due to the re-combination of the gases thus under a pressure of several atmospheres.

It would seem that it is difficult to start this action, but when once started it takes place freely and just about equals the quantity of gases generated, as the manometer showed no change; and each time a cell was added and more of the gases generated another and lower point of equilibrium was established.

#### PROPOSITION IV.

*The electro-motive force of a single liquid galvanic cell is equal to the excess of the affinity of the acid radical for one plate over its affinity for the other—these latter being measured in terms of electro-motive force.*

Suppose that into a cell containing dilute  $H_2SO_4$  we dip two strips of metal—one of zinc, the other of iron. Both begin to dissolve. As it is a synthetic process energy will be evolved, as we have seen, and, in fact, the liquid is heated. We connect the two strips of metal by a wire. The energy that formerly appeared as heat now appears as an electric current flowing from the plate, through the liquid, the other plate and the connecting wire.

But the two plates are sending their currents through the wire in opposite directions. Consequently the *sensible* current will be only the excess of one over the other.

By reference to the table (page 16) it will be seen that:

The electro-motive force of  $ZnSO_4 = 2.64$  volts.

" " " " "  $FeSO_4 = 2.01$  "

Excess over  $ZnSO_4$  over  $FeSO_4 = .63$

To test the trustworthiness of this result I made two small cells, filled with dilute  $H_2SO_4$ ,—one containing a platinum and a zinc plate, the other a platinum and an iron plate. Placing these in a circuit containing a galvanometer, but with their currents flowing in opposite directions through it, I found, as I expected, that the sensible current was that due to the platinum-zinc element, but its electro-motive force I did not try to determine.

Or again on the same principle:

The electro-motive force of  $\text{ZnSO}_4 = 2.64$  volts.

“ “ “ “ “  $\text{CuSO}_4 = 1.62$  “

$$\text{Excess of ZnSO}_4 \text{ over CuSO}_4 = 1.02$$

But this is the action of a Daniel cell. Though variously given, the electro-motive force of this element is, according to the best determinations, 1.079 volts.

Though not identical, the numbers are nearly enough so to prove that the principle is correct.

But in this case the copper does not pass into solution, for, as we have already seen, the attraction of  $\text{SO}_4$  is greater, for the hydrogen with which it is already united than it is for the copper, yet it is under a tendency so to unite up to the full amount of its affinity for it.

Hence, while no action takes place, a state of stress exists at the copper plate, and this stress exerts the same energy (1.62 volts) in cutting down the sensible current of the battery as though action did take place.

If we substitute platinum for copper we find that the electromotive force of the cell is still higher, but it is yet under 2.64 volts, showing that even for platinum  $\text{SO}_4$  has some affinity. Could a conductor be found which had absolutely no affinity for  $\text{SO}_4$ , the electromotive force of such an element, according to these determinations for  $\text{ZnSO}_4$ , would be 2.64 volts.

Thus we see the philosophy of an electro-motive series. And the metals named on page 16 may be arranged in the following order: K, Na, Mg, Zn, Cd, Fe, Cu, Hg, Ag.

When two plates of these metals are placed in  $\text{H}_2\text{SO}_4$  and connected by a wire, a current flows (in the liquid) from the one higher in the list to the one lower.

By a like study of the chlorides a similar series might be made out for these metals when placed in HCl, and it is easy to see that the two lists might not be entirely identical for all acids.

## SUPPLEMENTARY REMARKS ON THE ACTION OF BATTERIES.

A. The electro-motive force of  $\text{ZnSO}_4$  at  $18^\circ \text{C} = 2.64$  volts.

“ “ “ “ “  $\text{CuSO}_4$  at  $18^\circ = 1.62$  “

Difference at ordinary temperature = 1.02 "

The electro-motive force of $\text{ZnSO}_4$ at $94^\circ \text{C}$	= 2.31 volts.
" " " " $\text{CuSO}_4$ at $94^\circ$	= <u>1.36</u> "
" " " Difference at $94^\circ$	= .95 "

This would suggest that the electro-motive force of such a cell (Daniel's) would be lower at the boiling point than at the ordinary temperature.

So I made a small CuZn (unamalgamated) cell, placed it in a water bath and measured its electro-motive force at  $18^\circ \text{C}$  and  $96^\circ \text{C}$  in the same way that I measured the electro-motive force of the polarization current in the electrolytic cell.

I made this determination twice with the following results:

At ordinary temperature.

First trial, E. M. F. of cell	= .971 volt.
Second " " "	<u>.987</u> "
Mean	.979

As we have seen the theoretical number is 1.02 volts.

At  $94^\circ \text{C}$ .

First trial, E. M. F. of cell	= .938 volt.
Second " " "	<u>.949</u> "
Mean	.943

The theoretical number is .92 volts.

When we remember that all these data are experimental, consequently liable to error, the results will appear very satisfactory.

*B.* As we have seen in considering the theory of the method I used in my investigations, the numbers I obtained express the electro-motive force of the electric current generated by the combination of the separated ions.

In the electrolysis of water, either pure or acidulated, these ions are oxygen and hydrogen. Consequently we have something similar in principle to Grove's gas battery, and the E. M. F. of water, as I determined it, should be about equal to that of the gas battery.

For distilled water the E. M. F. is about 2.13 volts.

" acidulated " " " 1.80 " (page 23).

Sprague (page 224) gives the E. M. F. of Grove's gas battery at 1.50 volts, and quotes De la Rive, who states it to be 2.518 volts. I have not been able to find any statement on the subject in other authorities, but think it quite probable that Sprague is more nearly correct, as De la Rive wrote quite a while ago and was unacquainted with the exact methods of measurement used by physicists at present.

From what has been said it would be expected that the E. M. F. of the gas battery would vary anywhere between 1.80 and 2.13 volts, depending on the degree of acidulation of the water.

Two considerations may throw some light on the fact that the number given by Sprague is .3 of a volt lower than this minimum.

*First.* From what we have seen it would be expected that a slight pressure upon the gas would increase the E. M. F. of the battery, but beyond a certain point the E. M. F. would rapidly fall.

*Second.* In the study of the action of secondary batteries it has been found that the E. M. F. of the current they give is considerably less than that of the charging battery.

Something, possibly a molecular friction analogous to mechanical friction, seems to resist both the charging and discharging of the cell.

Now, as we have seen from the description of the method I used, the direct current from the battery was broken, and I measured the E. M. F. of the polarization current the next instant—catching it at its maximum. It is well-known that this current runs down rapidly.

These two considerations (and the second is the more important) probably explain the number stated by Sprague, but I recall no conditions that, upon this theory, would allow the electro-motive force to rise to the figure given by De la Rive.